TG: @Chalnaayaaar

02 Atomic Structure

Introduction

Atom is a Greek word and its meaning is indivisible i.e. an ultimate particle which cannot be further subdivided.

John Dalton considered that "all matters are composed of smallest indivisible particle called atom.

Dalton's Atomic Theory:

This theory is based on law of mass conservation and law of definite proportions. The salient features of this theory are:

(1) Each element is composed of extremely small particles called atoms.

(2) Atoms of a particular element are alike but differ from atoms of other element.

(3) Atom of each element is an ultimate particle and it has a characteristic mass but is structureless.

(4) Atoms are indestructible i.e. they can neither be created nor be destroyed.

(5) Atoms of different elements take part in chemical reaction to form molecule.

★ Golden Key Points ★

- Particles carrying negative charge were called negatrons by Thomson.The name negatron was changed to 'electron' by Stoney.

  In cathode ray experiment, particles (electron) forming the rays have same specific charge (e/m) which is independent of the nature of gas and electrode used. It points out that electrons are present in all atoms.

- Mass of electron is $\frac{1}{1837}$ times that of proton.

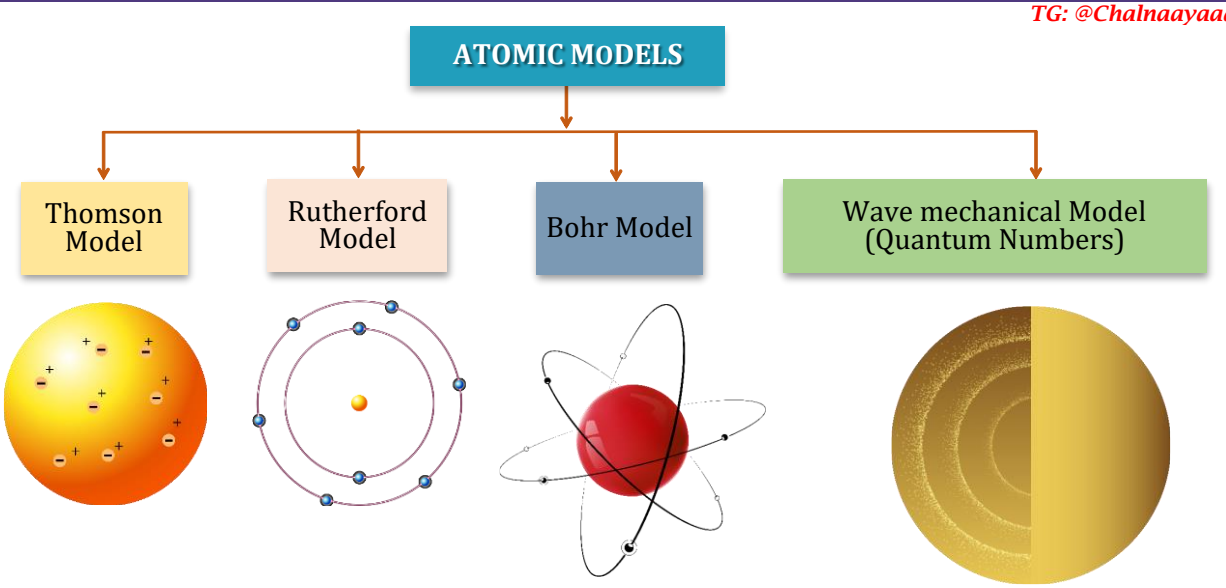
- Mass of moving electron = $\frac{\text{rest mass of electron}}{\sqrt{1-(v/c)^2}}$

  (Where v is the velocity of the electron and c is the velocity of light.)

  When $v = c \Rightarrow$ mass of electron = ∞ and if $v > c \Rightarrow$ mass of electron = imaginary

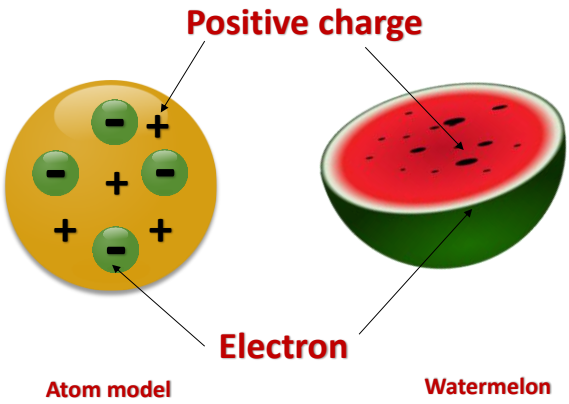
- In anode ray experiment, the particles forming rays have e/m value that is dependent on the nature of the gas taken in the discharge tube, i.e. +ve particles are different in different gases.

TG: @Chalnaayaaar



(A) Thomson's Model of Atom [1904]

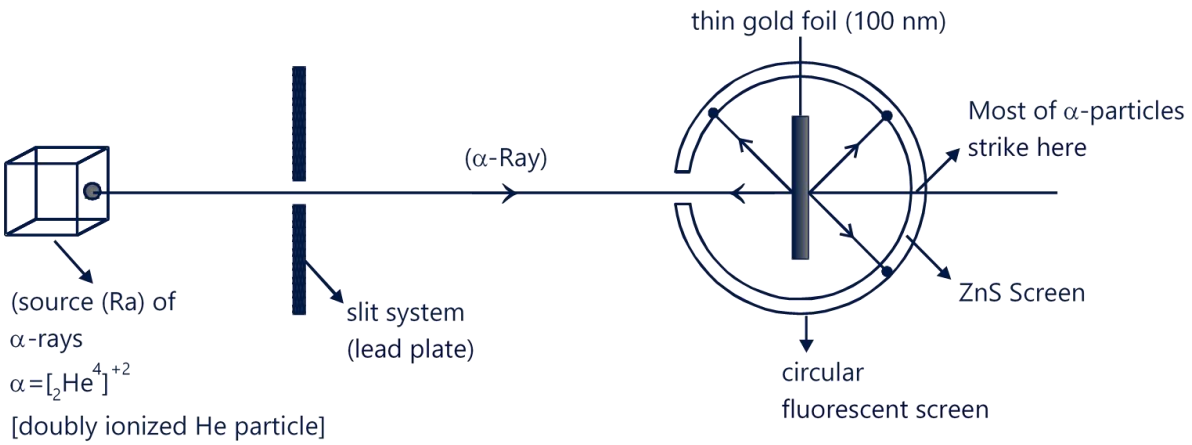
- Thomson was the first to propose a detailed model of the atom.
- Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are distributed more or less uniformly.
- This model of atom is known as "Plum-Pudding model" or "Raisin Pudding Model" or "Water Melon Model".



Drawbacks:

- An important drawback of this model is that the mass of the atoms is considered to be evenly spreaded over the atom.
- It is a static model. It does not reflect the movement of electron.

(B) Rutherford's Scattering Experiment



Rutherford observed that -

(i) Most of the α-particles passed through the gold foil undeflected.

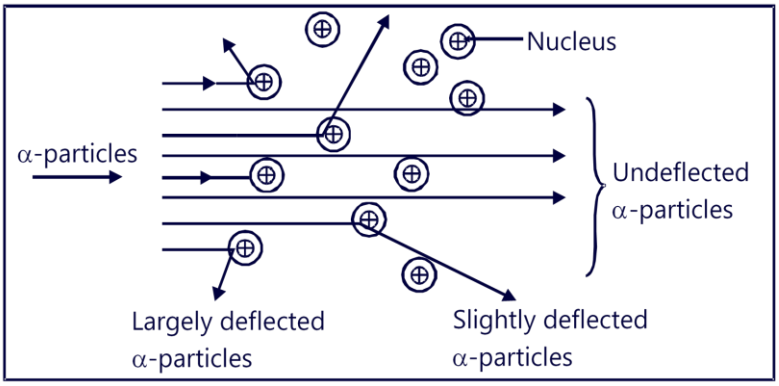
(ii) A small fraction of the α-particles were deflected by small angles.

(iii) A very few α-particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

Following conclusions were drawn from the above observations –

(i) Since most of the α-particles went straight through the metal foil undeflected, it means that there must be very large empty space within the atom.

(ii) Since few of the α-particles were deflected from their original paths through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.



- When α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.
- The positively charged heavy mass which occupies only a small volume in an atom is called nucleus. It is supposed to be present at the centre of the atom.

(iii) A very few of the α-particles suffered strong deflections or even returned on their path, indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

(C) Rutherford's atomic Model

On the basis of scattering experiments, Rutherford proposed model of the atom, which is known as nuclear atomic model. According to this model -

(i) An atom consists of a heavy positively charged nucleus where all the protons and neutrons are present. Protons & neutrons are collectively referred to as nucleons. Almost whole of the mass of the atom is contributed by these nucleons. The magnitude of the +ve charge on the nucleus is different for different atoms.

(ii) The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.

$$\frac{D_A}{D_N} = \frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5,\ D_A = 10^5\ D_N$$

Thus diameter (size) of the atom is 10^5 times the diameter of the nucleus.

- The radius of a nucleus is proportional to the cube root of the number of nucleons within it.

  $R \propto A^{1/3}$

  $\Rightarrow R = R_0 A^{1/3}$

  Where

  $R_0 = 1.33 \times 10^{-13}$ cm (constant)

  A = mass number (p + n)

  R = radius of the nucleus.

$$R = 1.33 \times 10^{-13} \times A^{1/3} \text{ cm}$$

(iii) There is an empty space around the nucleus called extra nuclear part. In this part electrons are present. The number of electrons in a neutral atom is always equal to number of protons present in the nucleus. As the nuclear part of atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume.

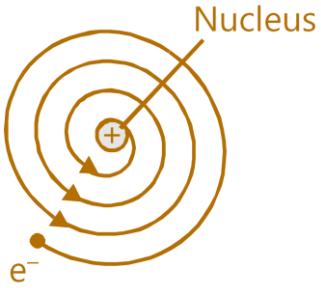
The volume of the atom is about 10^{15} times the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

- This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets.

Drawbacks of Rutherford's model:

(i) This theory could not explain the stability of atom. According to Maxwell, electron looses its energy continuously in the form of electromagnetic moving in circular path radiations. As a result of this, the e^- should loose energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable.



(ii) If the electrons loose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by electron is not continuous in an atom.

Atomic Number and Mass Number

(a) Atomic Number

It is represented by Z. The number of protons present in the nucleus is called atomic number of an element.

For neutral atom: Number of electrons = Number of protons

For an ion: Number of electrons = Z – (charge on ion)

Z = number of protons

TG: @Chalnaayaaar

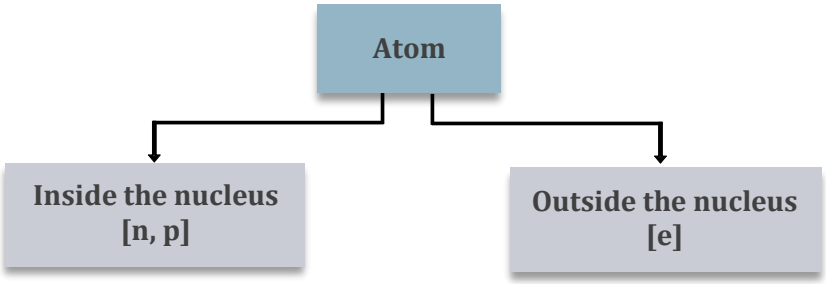
(b) Mass Number

It is represented by A. The sum of number of neutrons and protons is called the mass number of the element. It is also known as number of nucleons because neutrons & protons are present in nucleus.

Formula: A = number of protons + number of neutrons

Number of neutrons = A-Z

Note: A is always a whole number.



An atom of the element is represented by ${}^{A}_{Z}X$

Where, X = Symbol of element

Z = Atomic number = no. of protons = no. of electrons (If atom is neutral)

A = Mass number = no. of neutrons + no. of protons

eg. ${}_{11}Na^{+}$ ${}_{9}F^{-}$

$(p \rightarrow 11)$ $(p \rightarrow 9)$

$(e \rightarrow 10)$ $(e \rightarrow 9 + 1 = 10)$

eg. ${}^{12}_{6}C$ ${}^{16}_{8}O$

$p \rightarrow 6$ $p \rightarrow 8$

$n \rightarrow 12 - 6 = 6$ $n \rightarrow 16 - 8 = 8$

$e \rightarrow 6$ $e \rightarrow 8$

Mass no. [A] and atomic weight (amu = atomic mass unit)

Mass of Proton (m_p)	Mass of Neutron (m_n)	Mass of Electron (m_e)
1.672×10^{-27} kg **1.672×10^{-24} g** **1.00727 amu**	1.675×10^{-27} kg 1.675×10^{-24} g 1.00866 amu	9.1×10^{-31} kg 9.1×10^{-28} g 0.000549 amu

Method for Analysis of atomic weight →

eg. ${}^{12}_{6}C$

$p \rightarrow 6$ Weight of proton = 6×1.00727

$n \rightarrow 6$ Weight of neutron = 6×1.00866

$e \rightarrow 6$ $\frac{\text{Weight of electron} = 6 \times 0.000549}{\text{Weight of } {}^{12}_{6}C \text{ atom} = 12.099 \text{ amu}}$

Mass no. of ${}^{12}_{6}C$ atom = 12 [p and n]

Note: Mass no. of atom is always a whole no. but atomic weight may be in decimal.

TG: @Chalnaayaaar

Some Important Definitions

(a) **Isotopes:** They are atoms of a given element which have the same atomic number but differ in their mass numbers.

eg. • $^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$

• $^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$

• $^{1}_{1}H$, $^{2}_{1}H$, $^{3}_{1}H$

Explanation 1:

$^{12}_{6}C$	$^{13}_{6}C$	$^{14}_{6}C$
$p \rightarrow 6$	6	6
$e \rightarrow 6$	6	6
$n \rightarrow 6$	7	8

Note: Isotopes have the same number of protons but differ in the number of neutrons in the nucleus

Explanation 2:

$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$ (Radioactive element)
Protium (H)	Deuterium (D)	Tritium (T)
$p \rightarrow 1$	1	1
$e \rightarrow 1$	1	1
$n \rightarrow 0$	1	2

- Neutron is not available in Protium
- No. of Nucleons = No. of Neutrons + No. of Protons

  = n + p

Atomic Weight: The atomic weight of an element is the average of mass of all the isotopes of that element.

- If an element have three isotopes y_1, y_2 and y_3 and their isotopic weights are w_1, w_2, w_3 and their percentage/possibility/probability/ratio of occurrence in nature are x_1, x_2, x_3 respectively,

	Isotope (1)	Isotope (2)	Isotope (3)
Isotopes	y_1	y_2	y_3
Weights	w_1	w_2	w_3
Percentage Occurrence	x_1	x_2	x_3

Average atomic weight = $\frac{w_1x_1 + w_2x_2 + w_3x_3}{x_1 + x_2 + x_3}$

TG: @Chalnaayaaar

eg.	^{35}Cl		^{37}Cl
% Occurrence	75%		25%
or			
Ratio of occurrence	3	:	1

Average atomic weight $= \frac{35\times3+37\times1}{3+1} = \frac{142}{4} = 35.5$

(b) Isobars

Isobars are the atoms of different elements which have the same mass number but different atomic numbers i.e. they have different number of electrons, protons & neutrons but sum of number of neutrons & protons remains same.

Ex.1	$^{3}_{1}H$	$^{3}_{2}He$	**Ex.2**	$^{40}_{19}K$	$^{40}_{20}Ca$
	p = 1	p = 2		p = 19	p = 20
	e = 1	e = 2		e = 19	e = 20
	n = 2	n = 1		n = 21	n = 20
	p + n = 3	p + n = 3		n + p = 40	n + p = 40

(c) Isodiaphers

They are the atoms of different elements which have the same difference of the number of neutrons & protons.

Ex.1	$^{11}_{5}B$	$^{13}_{6}C$	**Ex.2**	$^{15}_{7}N$	$^{19}_{9}F$
	p = 5	p = 6		p = 7	p = 9
	e = 5	e = 6		e = 7	e = 9
	n = 6	n = 7		n = 8	n = 10
	n – p = 1	n – p = 1		n – p = 1	n – p = 1

(d) Isotones/Isoneutronic Species/Isotonic

They are the atoms of different elements which have the same number of neutrons.

Ex.1	$^{3}_{1}H$	$^{4}_{2}He$	**Ex. 2**	$^{39}_{19}K$	$^{40}_{20}Ca$
	p = 1	p = 2		p = 19	p = 20
	e = 1	e = 2		e = 19	e = 20
	n = 2	n = 2		n = 20	n = 20

(e) Isosters

They are the molecules which have the same number of atoms & electrons.

Ex.1	CO_2	N_2O	**Ex.2**	CaO	KF
	Atoms = 1 + 2	Atoms = 2 + 1		Atoms = 2	Atoms = 2
	= 3	= 3		Electrons = 20 + 8	Electrons = 19 + 9
	Electrons = 6 + 8 × 2	Electrons = 7 × 2 + 8		= 28 e	= 28 e
	= 22 e	= 22e			

TG: @Chalnaayaaar

(f) Isoelectronic Species

They are the atoms, molecules or ions which have the same number of electrons.

Ex.1	**Cl^-**	**Ar**
	18 e	18 e
Ex.2	**H_2O**	**NH_3**
	(2 + 8) = 10 e	(7 + 3) = 10 e
Ex.3	**BF_3**	**SO_2**
	(5 + 9 × 3) = 32 e	(16 + 8 × 2) = 32 e

★ Golden Key Points ★

- Isotopes have same chemical property but different physical property.
- Isotopes do not have the same value of e/m.
- Isobars do not have the same chemical & physical property.
- Isobars do not have the same value of e/m
- For isotones, $A_1 - Z_1 = A_2 - Z_2$
- For isodiapheres, $A_1 - 2Z_1 = A_2 - 2Z_2$

Illustration 1:

If the mass of neutron is doubled & mass of electron is halved then find out the new atomic mass of $^{12}_{6}C$ and the percent by which it is changed.

Solution:

Step-1 $^{12}_{6}C \rightarrow$ e = 6

p = 6 = 6 amu
n = 6 = 6 amu] =12 amu

If the mass of neutron is doubled and mass of electron is halved then,

n = 12 amu
p = 6 amu] = 18 amu

Note: mass of electron is negligible, so it is not considered in atomic mass.

Step-2 % Increment = $\frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 = \frac{18-12}{12} \times 100 = 50\%$

Illustration 2:

If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled then find out the new atomic weight of $^{12}_{6}C$.

Solution:

Step-1 $^{12}_{6}C \rightarrow$ p = 6
n = 6] = 12 amu

If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled, then new atomic mass will be:

n = 12 amu
p = 3 amu] =15 amu

Step-2 % Increment = $\frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 = \frac{15-12}{12} \times 100 = 25\%$

Illustration 3:

If no. of protons in X^{-2} is 16. then no. of electrons in X^{+2} will be –

(1) 14 (2) 16 (3) 18 (4) None

Solution:

No. of protons in X^{-2} is = 16

No. of electrons in X^{+2} is = 14

Illustration 4:

Assuming that atomic weight of $^{12}_{6}C$ is 150 units from atomic table, then according to this assumption, the weight of $^{16}_{8}O$ will be:

Solution:

$\because$ 12 amu =150 units

$\therefore$ 1 amu = $\frac{150}{12}$ units

$\therefore$ 16 amu = $\frac{150}{12} \times 16 = 200$ Units

Illustration 5:

An element have three isotopes and their isotopic weights are 11, 12, 13 unit and their percentage of occurrence in nature is 85, 10, 5 respectively, then calculate the average atomic weight of element.

Solution:

Average Atomic weight = $\frac{11\times85+12\times10+13\times5}{85+10+5} = \frac{935+120+65}{100}$

Average atomic weight = $\frac{1120}{100} = 11.2$

Illustration 6:

Average atomic weight of an element M is 51.7. If two isotopes of M are ^{50}M and ^{52}M, then calculate the percentage of occurrence of ^{50}M in nature.

Solution:

^{50}M		^{52}M
x_1	+	$x_2 = 100$
		$x_2 = (100 - x_1)$

average atomic weight = $\frac{w_1x_1+w_2x_2}{x_1+x_2} = 51.7 = \frac{50\times x_1+52\times x_2}{x_1+x_2}$

$51.7 = \frac{50x_1+52(100-x_1)}{x_1+(100-x_1)}$

$5170 = 50\,x_1 + 5200 - 52x_1$

$5170 = -2x_1 + 5200$

$2x_1 = 30$

$x_1 = 15$

$^{50}M = 15\%$ $52M = 85\%$

BEGINNER'S BOX-1

1. Which of the following statements is incorrect for anode rays?

(1) They are deflected by electric and magnetic fields.

(2) Their e/m ratio depends on the gas in the discharge tube used to produce the anode rays.

(3) The e/m ratio of anode rays is constant.

(4) They are produced by the ionisation of the gas in the discharge tube.

2. Which of the following pairs have identical value of e/m?

(1) A proton and a neutron (2) A proton and deuteron

(3) Deuteron and an α – particle (4) An electron and γ – rays

3. Rutherford's α – particle scattering experiments led to the conclusion that

(1) mass and energy are related together

(2) the mass and the positive charge of an atom are concentrated in the nucleus

(3) neutrons are present in the nucleus

(4) atoms are electrically neutral

4. The radius of nucleus $^{27}_{13}Al$ will be

(1) 1.2×10^{-15} m (2) 2.7×10^{-15} m (3) 10.8×10^{-15} m (4) 4×10^{-15} m

5. Which of the following elements has maximum density of nucleus.

(1) $^{30}_{14}SO$ (2) $^{31}_{15}P$ (3) $^{16}_{8}O$ (4) All have same density

6. Select iso electronic set :-

(a) Na^+, H_3O^+, NH_4^+ (b) CO_3^{-2}, NO_3^-, H_2CO_3 (c) P^{-3}, HCl, $C_2H_5^-$, PH_3 (d) F^-, Ne, Na^+

(1) a, b, d (2) b, c, d (3) a, b, c (4) a, b, c, d

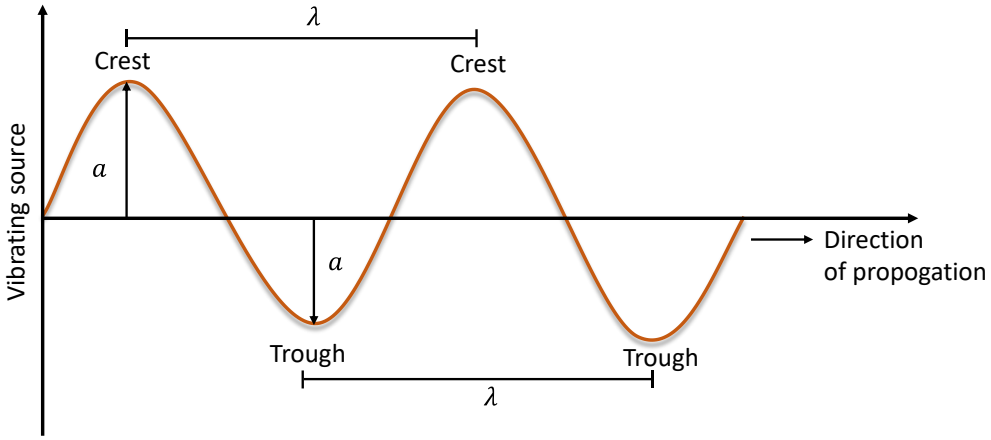
7. If the table of atomic masses were established with respect to oxygen atom and its assigned value of atomic mass to be 100, then the mass of carbon atom would be, approximately:-

(1) 24 (2) 75 (3) 50 (4) 112

Electromagnetic Waves (EM Waves) or Radiant Energy

According to this theory, the energy is transmitted from one body to another in the form of waves and these waves travel in the space with the same speed as light (3×10^8 m/s). These waves are known as Electro-magnetic waves or radiant energy. **Ex:** Radio waves, micro waves, Infra-red rays, visible rays, ultraviolet rays, X–rays, gamma rays.

- The radiant energy does not need any medium for propagation.
- The radiant energy has electric and magnetic fields perpendicular to each other and travel at right angle to these fields.
- The upper most point of the wave is called crest and the lower most point is called trough.



Some of the terms employed in dealing with the waves are described below.

(1) **Wavelength (λ) (Lambda) :** It is defined as the distance between two nearest crests or troughs.

It is measured in terms of Å (Angstrom), pm (picometre), nm (nanometre), cm(centimetre), m (metre)

$1Å = 10^{-10}$ m, 1 pm $= 10^{-12}$ m, 1nm $= 10^{-9}$ m, 1cm $= 10^{-2}$m

(2) **Wave number ($\bar{\nu}$) (nu bar):** It is the reciprocal of the wavelength, that is number of waves present in unit length $\boxed{\bar{\nu} = \frac{1}{\lambda}}$

It is measured in terms of cm^{-1}, m^{-1} etc.

(3) **Frequency (ν) (nu):** Frequency of a wave is defined as the number of waves which pass through a point in 1 s. It is measured in terms of hertz (Hz), s^{-1} or cycle/s(cps) (1 hertz = 1 s^{-1})

(4) **Time period (T):** Time taken by a wave to pass through one point. $\boxed{T = \frac{1}{\nu}\text{second}}$

(5) **Velocity (c):** Velocity of a wave is defined as distance covered by a wave in 1 second

$c = \lambda/T = \lambda\nu$ or $\nu = c/\lambda$ or $c = \nu\ (s^{-1}) \times \lambda\ (m)$ or $c = \nu\lambda\ (m\ s^{-1})$

Since c is constant i.e. frequency is inversely proportional to λ

(6) **Amplitude (a):** The amplitude of a wave is defined as the height of crest or depth of trough.

Important note: $\boxed{\nu = \frac{c}{\lambda} = c\bar{\nu}}$ $\left(\bar{\nu} = \frac{1}{\lambda}\right)$

Electromagnetic spectrum or EM spectrum:

The arrangement obtained by arranging various types of EM waves in order of their increasing frequency or decreasing wavelength is called as EM SPECTRUM

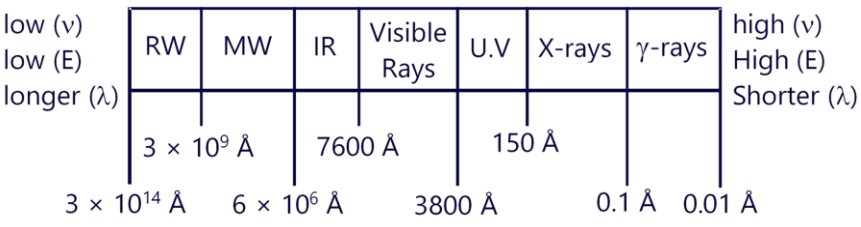


Illustration 7:

The Vividh Bharti station of All India Radio broadcasts on a frequency of 1368 kilo hertz. Calculate the wavelength of the electromagnetic waves emitted by the transmitter.

Solution:

As we know velocity of light (c) = 3×10^8 m/s

Given ν (frequency) = 1368 kHz = 1368×10^3 Hz = 1368×10^3 s^{-1}

$\because \lambda = \frac{c}{\nu}$ $\quad\quad$ $\therefore \lambda = \frac{3\times10^8 m s^{-1}}{1368\times10^3 s^{-1}} = 219.3$ m

Illustration 8:

Calculate $\bar{\nu}$ in cm^{-1} and ν of yellow radiation having a wavelength of 5800 Å

Solution:

As we known $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800Å} = \frac{1}{5800\times10^{-8} cm} = \frac{10^8}{5800}$ cm^{-1} = 17241.37 cm^{-1}

$\nu = c\bar{\nu}$ = 3×10^{10} cm $s^{-1} \times 1.7 \times 10^4$ cm^{-1} = $3 \times 1.7 \times 10^{14}$ = 5.1×10^{14} s^{-1}

Illustration 9:

A particular radiostation broadcast at a frequency of 1120 kilo hertz. Another radio station broadcast at a frequency of 98.7 mega hertz. What are the wavelength of radiations from each station?

Solution:

Station 1st $\lambda = \frac{c}{\nu} = \frac{3\times10^8 m s^{-1}}{1120\times10^3 s^{-1}}$ = 267.86 m

Station 2nd $\lambda = \frac{c}{\nu} = \frac{3\times10^8 m s^{-1}}{98.7\times10^6 s^{-1}}$ = 3.0395 m

Illustration 10:

How long would it take a radio wave of frequency 6×10^3 s^{-1} to travel from mars to earth, that is a distance of 8×10^7 km?

Solution:

$\because$ Distance to be travelled from mars to earth = 8×10^7 km = 8×10^{10} m

$\therefore$ Velocity of EM waves = 3×10^8 m/s

$\therefore$ Time = $\frac{\text{Distance}}{\text{Velocity}} = \frac{8\times10^{10} m}{3\times10^8 m/s}$ = 2.66×10^2 s = 4 min 26 s

Planck's Quantum Theory

According to Planck's quantum theory:

(1) The radiant energy emitted or absorbed by a body is not continuous but discontinuous in the form of small discrete packets of energy and these packets are called quanta.

(2) In case of light, the smallest packet of energy is called as 'photon' but in general case the smallest packet of energy is called as quantum.

(3) The energy of each quantum is directly proportional to frequency of the radiation i.e.

$E \propto \nu$ $\quad\Rightarrow\quad$ $E = h\nu$ $\quad$ or $\quad$ $E = \frac{hc}{\lambda}$ $\left\{\because \nu = \frac{c}{\lambda}\right\}$

where,
h is proportionality constant or Planck's constant
$h = 6.626 \times 10^{-37}$ kJ s **or**
$h = 6.626 \times 10^{-34}$ J s **or**
$h = 6.626 \times 10^{-27}$ erg s

(4) Total amount of energy transmitted from one body to another will be some integral multiple of energy of a quantum. $E = nh\nu = \frac{nhc}{\lambda} = nhc\bar{\nu}$

where n = Positive integer
= Number of quanta

Illustration 11:

Calculate the energy (in joule) of a photon of sodium light of wave length 5.862×10^{-16} m.

Solution:

$\lambda = 5.862 \times 10^{-16}$ m, $c = 3 \times 10^8$ m s^{-1}

$E = nh\nu$ or $\frac{nhc}{\lambda}$ $\{\therefore n = 1\}$

$$\therefore E = \frac{hc}{\lambda} = \frac{1 \times 6.6 \times 10^{-34}\,J\,s \times 3 \times 10^8\,m\,s^{-1}}{5.862 \times 10^{-16}\,m} = \frac{6.6 \times 3}{5.862} \times 10^{-10}\,J = 3.38 \times 10^{-10}\,J$$

Illustration 12:

Calculate the frequency & energy of a photon of wave length 5000 Å.

Solution:

(a) Calculation of frequency: $\lambda = 5000$ Å $= 5000 \times 10^{-10}$ m

$$\because \quad \nu = \frac{c}{\lambda} = \frac{3 \times 10^8\,m/s}{5 \times 10^{-7}\,m} = 0.6 \times 10^{-15}\,s^{-1} = 6 \times 10^{14}\,s^{-1}$$

(b) Calculation of energy:

$E = h\nu = 6.626 \times 10^{-34}$ joule second $\times 6 \times 10^{14}\,s^{-1} = 3.97 \times 10^{-19}$ joule

Illustration 13:

Calculate the λ and frequency of a photon having an energy of 2 electron volt

Solution:

$\because$ $1eV = 1.602 \times 10^{-19}$ J $\therefore$ $2eV = 3.204 \times 10^{-19}$ J = E

(a) Calculation of wavelength (λ):

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\,Js \times 3 \times 10^8\,m\,s^{-1}}{3.204 \times 10^{-19}\,J} = 6.204 \times 10^{-7}\,m$$

(b) Calculation of frequency (ν):

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8\,m\,s^{-1}}{6.204 \times 10^{-7}\,m} = 0.49 \times 10^{15}\,s^{-1} = 4.9 \times 10^{14}\,s^{-1}$$

Illustration 14:

Which has a higher energy?

(a) A photon of violet light with wave length 4000 Å

(b) A photon of red light with wave length 7000 Å

Solution:

(a) Violet light:

$$E_{violet} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{4000\times10^{-10}\,m} = 4.97 \times 10^{-19} \text{ joule}$$

(b) Red light:

$$E_{red} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{7000\times10^{-10}\,m} = 2.8 \times 10^{-19} \text{ joule}$$

So, $E_{violet} > E_{red}$

BEGINNER'S BOX-2

1. Electromagnetic radiation travels through vacuum at a speed of

(1) 186000 m/s (2)125 m/s

(3) 3.00×10^{8} m/s (4) It depends upon wavelength

2. What is the wavelength (Å) of a photon that has an energy of 4.38×10^{-18} J

(1) 454 Å (2) 2.3×10^{7} Å (3) 6.89×10^{15} Å (4) 1.45×10^{-15} Å

3. A 1kw radio transmitter operates at a frequency of 800 Hz.How many photons per second does it emit?

(1) 1.71×10^{21} (2) 1.88×10^{33} (3) 6.02×10^{23} (4) 2.85×10^{20}

Bohr's Atomic Model

- This model was based on quantum theory of radiation and classical laws of physics.
- Bohr model is applicable only for single electron species like H, He^{+}, Li^{2+} etc.
- Bohr model is based on particle nature of electron.

Some Important formulae:

$$\text{Coulombic force} = \frac{Kq_1q_2}{r^2}$$

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

$$\text{Angular momentum} = mvr$$

Important postulates:

1st Postulate:

- Atom has a nucleus where all protons and neutrons are present.
- The size of nucleus is very small and it is present at the centre of the atom.

2nd Postulate:

- Negatively charged electron revolve around the nucleus in the same way as the planets revolve around the sun.
- The path of electron is circular.
- The attraction force (Coulombic or electrostatic force) between nucleus and electron is equal to the centrifugal force on electron.
- i.e. Attraction force towards nucleus = centrifugal force away from nucleus.

3rd Postulate:

- Electrons can revolve only in those orbits in which angular momentum (mvr) of electron is integral multiple of $\frac{h}{2\pi}$

  i.e. $mvr = \frac{nh}{2\pi} = n\hbar$ $\qquad \hbar = \frac{h}{2\pi}$

  where: n = + ve integer number (n = 1,2,3,4, ...)

  h = Planck's constant

- Angular momentum can have values such as $\frac{h}{2\pi}, 2\frac{h}{2\pi}, 3\frac{h}{2\pi}, 4\frac{h}{2\pi}, 5\frac{h}{2\pi}$ ..... but cannot have fractional values such as $1.5\frac{h}{2\pi}, 1.2\frac{h}{2\pi}, 0.5\frac{h}{2\pi}$ .....

4th Postulate:

- The orbits in which electron can revolve are known as stationary orbits because in these orbits energy of electron is always constant.

5th Postulate:

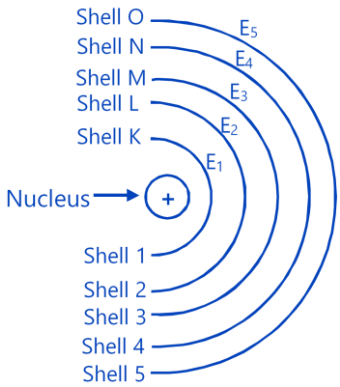
- Each stationary orbit is associated with definite amount of energy therefore these orbits are also called as energy levels and are numbered as 1, 2, 3, 4, 5, ... or K, L, M, N, O, ... from the nucleus outwards.

6th Postulate

- The emission or absorption of energy in the form of photon can only occur when electron jumps from one stationary state to another & it is

  $\Delta E = E_{higher} - E_{lower} = E_{n_2} - E_{n_1}$ = Energy of a quantum

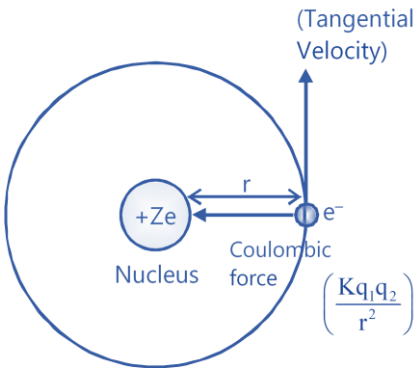
  = $h\nu$



- Energy is absorbed when electron jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.
- $n_2 > n_1$ whether emission or absorption of energy will occur.

Application of Bohr's Model

(A) Radius of Various Orbits (Shell)



Coulombic force = $\frac{Kq_1q_2}{r^2}$

$= \frac{K.Ze.e}{r^2} = \frac{KZe^2}{r^2}$

Where $K = 9 \times 10^9\ Nm^2/coulomb^2$

As we know – Coulombic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \quad \text{or} \quad v^2 = \frac{KZe^2}{mr} \qquad .....(1)$$

Also, $$mvr = \frac{nh}{2\pi} \quad \text{or} \quad v = \frac{nh}{2\pi mr} \qquad .....(2)$$

Putting the value of v from eqn. (2) to eqn. (1)

$$\left(\frac{nh}{2\pi mr}\right)^2 = \frac{KZe^2}{mr} \text{ or } \frac{n^2h^2}{4\pi^2m^2r^2} = \frac{KZe^2}{mr}$$

$$r = \frac{n^2h^2}{4\pi^2 m KZe^2} \qquad .....(3)$$

Putting the value of π, h, m, K, & e (Constants) in the above eqn. (3)

$r = 0.529 \times 10^{-8} \times \frac{n^2}{Z}$ cm $\qquad \{1\ Å = 10^{-10}\ m = 10^{-8}\ cm\}$

$$r_n = 0.529 \times \frac{n^2}{Z}\ Å$$

This formula is only applicable for hydrogen and hydrogen like species i.e. species containing single electron.

(B) Velocity of an electron

Since coulombic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \quad \text{or} \quad v^2 = \frac{KZe^2}{mr} \qquad .....(1)$$

Putting the value of Angular momentum

$$mvr = \frac{nh}{2\pi} \quad \text{or} \quad KZe^2 = \frac{nh}{2\pi}(v)$$

$$v = \frac{2\pi KZe^2}{nh}$$

Putting the value of π, k, e & h $\quad v = 2.188 \times 10^6 \frac{Z}{n} m/s$

TG: @Chalnaayaaar

(C) Time period (T_n)

Time taken for complete revolution in n^{th} orbit

$$= \frac{\text{Distance}}{\text{Velocity}} = \frac{2\pi r_n}{V_n}$$

$$\left(T_n \propto \frac{n^3}{z^2} \right)$$

(D) Frequency of Revolution (ν_n)

Number of revolutions per unit time in n^{th} orbit

$$= \frac{\text{Velocity}}{\text{Distance}} = \frac{V_n}{2\pi r_n}$$

$$\left(\nu_n \propto \frac{z^2}{n^3} \right)$$

Illustration 15:

Calculate the radius of 1st, 2nd, 3rd, 4th Bohr's orbit of hydrogen.

Solution:

Radius of Bohr's orbit: $r = 0.529 \times \frac{n^2}{Z}$ Å

(a) Radius of I orbit : $r = 0.529 \times \frac{1^2}{1}$ Å = 0.529 Å

(b) Radius of II orbit : $r = 0.529 \times \frac{2^2}{1} = 0.529 \times 4 = 2.116$ Å

(c) Radius of III orbit : $r = 0.529 \times \frac{3^2}{1} = 0.529 \times 9 = 4.761$ Å

(d) Radius of IV orbit : $r = 0.529 \times \frac{4^2}{1} = 0.529 \times 16 = 8.464$ Å

Illustration 16:

Calculate the radius ratio of 3rd & 5th orbit of He^+.

Solution:

$\because$ $r = 0.529 \times \frac{n^2}{Z}$ Å and Atomic Number of He = 2

$\therefore$ $r_3 = 0.529 \times \frac{(3)^2}{2} = 0.529 \times \frac{9}{2}$ and $r_5 = 0.529 \times \frac{(5)^2}{2} = 0.529 \times \frac{25}{2}$

Therefore $\frac{r_3}{r_5} = \frac{0.529 \times \frac{(3)^2}{2}}{0.529 \times \frac{(5)^2}{2}}$ or $r_3 : r_5 = 9 : 25$

TG: @Chalnaayaaar

Illustration 17:

Calculate the radius ratio of 2nd orbit of hydrogen and 3rd orbit of Li^{+2}.

Solution:

Atomic number of H = 1, Atomic number of Li = 3,

2nd orbit radius of Hydrogen $(r_2)_H = 0.529 \times \frac{2^2}{1}$

3rd orbit radius of Li^{+2} $(r_3)_{Li^+} = 0.529 \times \frac{3^2}{3}$

$$\because \frac{(r_2)_H}{(r_3)_{Li^{+2}}} = \frac{0.529 \times \frac{2^2}{1}}{0.529 \times \frac{3^2}{3}} = \frac{4}{3} \quad \Rightarrow \quad \therefore (r_2)_H : (r_3)_{Li^{+2}} = 4 : 3$$

Illustration 18:

Calculate the radius ratio of 2nd excited state of H & 1st excited state of Li^{+2}

Solution:

2nd excited state, means e^- is present in 3rd shell of hydrogen

$$r_3 = 0.529 \times \frac{(3)^2}{1} = 0.529 \times 9$$

1st excited state, means e^- is present in 2nd shell of Li^{+2}

$$r_2 = 0.529 \times \frac{(2)^2}{3} = 0.529 \times \frac{4}{3}$$

$$\frac{\text{radius of } 2^{nd} \text{ excited state of hydrogen}}{\text{radius of } 1^{st} \text{ excited state of } Li^{+2}} = \frac{(r_3)_H}{(r_2)_{Li^{+2}}} = \frac{0.529 \times \frac{9}{1}}{0.529 \times \frac{4}{3}} = \frac{27}{4}$$

Illustration 19:

Calculate velocity of an electron present in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.

Solution:

Velocity of electron in 3rd orbit:

$$\because \quad V_n = 2.188 \times 10^6 \times \frac{Z}{n} \text{ ms}^{-1}$$

$$\therefore \quad V_3 = 2.188 \times 10^6 \times \frac{1}{3} \text{ ms}^{-1} = 7.29 \times 10^5 \text{ ms}^{-1}$$

No. of revolution per second

$$= \frac{v_n}{2\pi r_3} = \frac{v_n}{2\pi\left(\frac{n^2 a_0}{z}\right)} = \frac{7.29 \times 10^5}{2 \times 3.14 \times 9 \times 0.529 \times 10^{-10}} = 2.44 \times 10^{14} \text{ r.p.s.}$$

Illustration 20:

How much time an e^- will take for one complete revolution in 2nd orbit of He^+?

Solution:

$$\text{Time taken} = \frac{\text{distance}}{\text{velocity}}$$

$$= \frac{2\pi r}{v} = \frac{2\times 3.14\times 0.529\times \frac{4}{2}\times 10^{-10}\,m}{2.18\times 10^{6}\times \frac{2}{2}\,ms^{-1}} = 3.05\times 10^{-16}\,s$$

Energy of an electron

Let the total energy of an electron be E. It is the sum of kinetic and potential energy.

i.e. E = K.E.+ P.E.

$$E = \left(\frac{1}{2}mv^2\right)+\left(\frac{Kq_1q_2}{r}\right) \qquad \left[P.E. = -\frac{KZe^2}{r}\right]$$

$$E = \frac{1}{2}mv^2 + \frac{K.Ze.(-e)}{r} = \frac{1}{2}mv^2 - \frac{KZe^2}{r} \qquad \left[KE = \frac{1}{2}mv^2 = \frac{KZe^2}{2r}\right]$$

$$E = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

Putting the value of r from eq. (3)

$$E_n = -\frac{KZe^2\times 4\pi^2 mKZe^2}{2n^2h^2} \quad \text{or} \quad \boxed{E_n = -\frac{2\pi^2 mK^2Z^2e^4}{n^2h^2}}$$

Putting the value of π, K, e, m, h, we get:

$$\boxed{E_n = -2.18\times 10^{-18}\times\frac{Z^2}{n^2}\,J/atom} \quad \text{or} \quad \boxed{E_n = -13.6\times\frac{Z^2}{n^2}\,eV/atom}$$

This formula is applicable for hydrogen atom & hydrogen like species i.e. single electronic species.

Since n can have only integral values, it follows that total energy of the e^- is quantised.

The –ve sign indicates that the electron is bounded towards nucleus.

Some extra points:

(i) $K.E = \frac{KZe^2}{2r}$ i.e. $K.E. \propto \frac{1}{r}$ On increasing radius, K.E. decreases.

(ii) $P.E. = -\frac{KZe^2}{r}$ i.e. $P.E. \propto -\frac{1}{r}$ On increasing radius, P.E. increases.

(iii) $E = -\frac{KZe^2}{2r}$ i.e. $E. \propto -\frac{1}{r}$ On increasing radius, total energy increases.

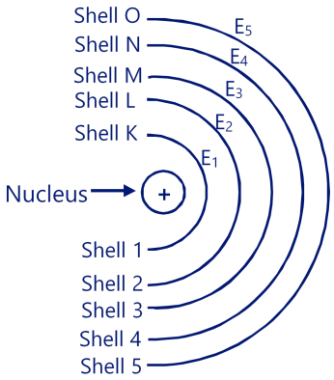
Conclusion: P.E. = (–) 2KE | KE = (–) E | P.E = 2E

Energy difference between two energy levels: $E_{n_2} - E_{n_1} = -13.6\times Z^2\left[\frac{1}{n_2^2}-\frac{1}{n_1^2}\right]$

Energy level for H atom can be represented as follows:

n = 6 or P	$E_6 = -0.38$ eV	
n = 5 or O	$E_5 = -0.54$ eV	
n = 4 or N	$E_4 = -0.85$ eV	$E_5 - E_4 = 0.31$ eV
n = 3 or M	$E_3 = -1.51$ eV	$E_4 - E_3 = 0.66$ eV
n = 2 or L	$E_2 = -3.4$ eV	$E_3 - E_2 = 1.89$ eV
n = 1 or K	$E_1 = -13.6$ eV	$E_2 - E_1 = 10.2$ eV

i.e. $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4)$ .....



Important Definitions:

(i) Ionization energy:

Minimum amount of energy required to eject an electron from the ground state of an isolated atom is called as ionization energy.

$n_1 = 1$; $n_2 = \infty$

(ii) Separation energy:

Minimum energy required to escape out electron from its excited state is called as separation energy.

$n_1 = 2, 3, 4, 5, \ldots$; $n_2 = \infty$

(iii) Excitation energy:

Amount of energy required to shift an electron from ground state to any excited state is called as excitation energy.

$n_1 = 1$; $n_2 = 2, 3, 4, 5, \ldots\ldots$

Note: All these kinds of energy are always positive.

Illustration 21:

If the total energy of an electron is –1.51 eV in hydrogen atom then find out K.E, P.E, orbit's radius and velocity of the electron in that orbit.

Solution:

(i) K.E = – E = 1.51 eV

(ii) PE = 2 × E = – 2 × 1.51 = – 3.02 eV

(iii) $\because \quad E = -13.6 \times \frac{z^2}{n^2} eV$

or $\quad -1.51 = -13.6 \times \frac{1^2}{n^2}$

$\Rightarrow \quad n^2 = \frac{-13.6}{-1.51} = 9$

$\therefore \quad n = 3$ i.e. 3rd orbit

(iv) $r = 0.529 \times \frac{n^2}{Z}$

$= 0.529 \times \frac{3 \times 3}{1} = 0.529 \times 9 = 4.761 Å$

(v) $v = 2.188 \times 10^8 \times \frac{Z}{n}$

$= 2.188 \times 10^8 \times \frac{1}{3}$ cm/s $= 0.729 \times 10^8$ cm/s

TG: @Chalnaayaaar

Illustration 22:

Calculate the energy of Li^{+2} ion for 2nd excited state

Solution:

$E = -13.6 \times \frac{Z^2}{n^2}$ $\because$ Z = 3 and electron present in 2nd excited state, means electron present in 3rd shell

i.e. n = 3

$\therefore \quad E = -13.6 \times \frac{(3)^2}{(3)^2} = -13.6$ eV/atom

Illustration 23:

Calculate the ratio of energies of He^+ for 1st & 2nd excited state.

Solution:

$$\frac{\text{Energy of } (He^+)\ 1^{st}\ \text{Excited state}}{\text{Energy of } (He^+) 2^{nd}\ \text{Excited state}} = \frac{\text{Energy of } (He^+) 2^{nd}\ \text{shell}}{\text{Energy of } (He^+) 3^{rd}\ \text{shell}}$$

$$= \frac{-13.6 \times \frac{(2)^2}{(2)^2}}{-13.6 \times \frac{(2)^2}{(3)^2}} = \frac{9}{4}$$

Illustration 24:

The ionization energy for the hydrogen atom is 13.6 eV then the required energy in eV to excite it from the ground state to 1st excited state

Solution:

Ionization energy = 13.6 eV

i.e. Energy in ground state = –13.6 eV

Energy of Ist excited state

i.e. 2nd orbit = –3.4 eV

so, $E_2 - E_1 = -3.4 + 13.6 = 10.2$ eV

★ Golden Key Points ★

- Bohr's atomic model is applicable only for monoelectronic species like H, He^+, Li^{+2}, Na^{10+}, U^{91+} etc.

$$E_{z,n} = E_H = \frac{Z^2}{n^2}$$

if z is same	if n is same
$E_n = E_H \times \frac{1}{n^2}$	$E = E_H \times z^2$

TG: @Chalnaayaaar

BEGINNER'S BOX-3

1. In which of the following is the radius of the first orbit minimum ?

(1) A Hydrogen atom (2) A tritium atom

(3) Triply ionized beryllium (4) Double ionized helium

2. The energy needed to excite a hydrogen atom from its ground to its third excited state is

(1) 12.1 eV (2) 10.2 eV (3) 0.85 eV (4) 12.75 eV

3. The ionisation energy of a hydrogen atom is 13.6 ev. The energy of the ground level in doubly ionised lithium is

(1) –28.7 eV (2) –54.4 eV (3) –122.4 eV (4) –13.6 eV

4. What would be the radius of 2^{nd} excited state in Li^{+2} ion ?

(1) 0.529 Å (2) 1.59 Å (3) 0.2645 Å (4) 0.5299 Å

5. 2^{nd} separation energy of an electron in H atom

(1) 27.2 eV (2) 1.51 eV (3) 3.4 eV (4) 13.6 eV

6. How much energy would be required by an electron while moving from ground state to 3^{rd} excited state of He^{+} ion.

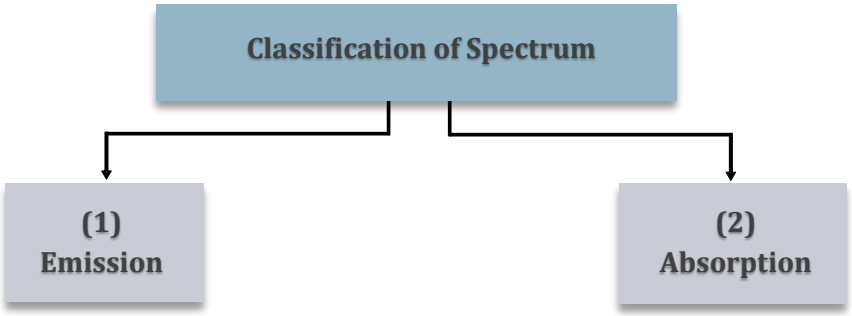
(1) 40.8 eV (2) 10.2 eV (3) 51 eV (4) 48.35 eV

7. Bohr's theory is not applicable to

(1) He (2) Li^{+2} (3) He^{+} (4) H atom

Spectrum

When a radiation is passed through a spectroscope (prism) for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the given radiation

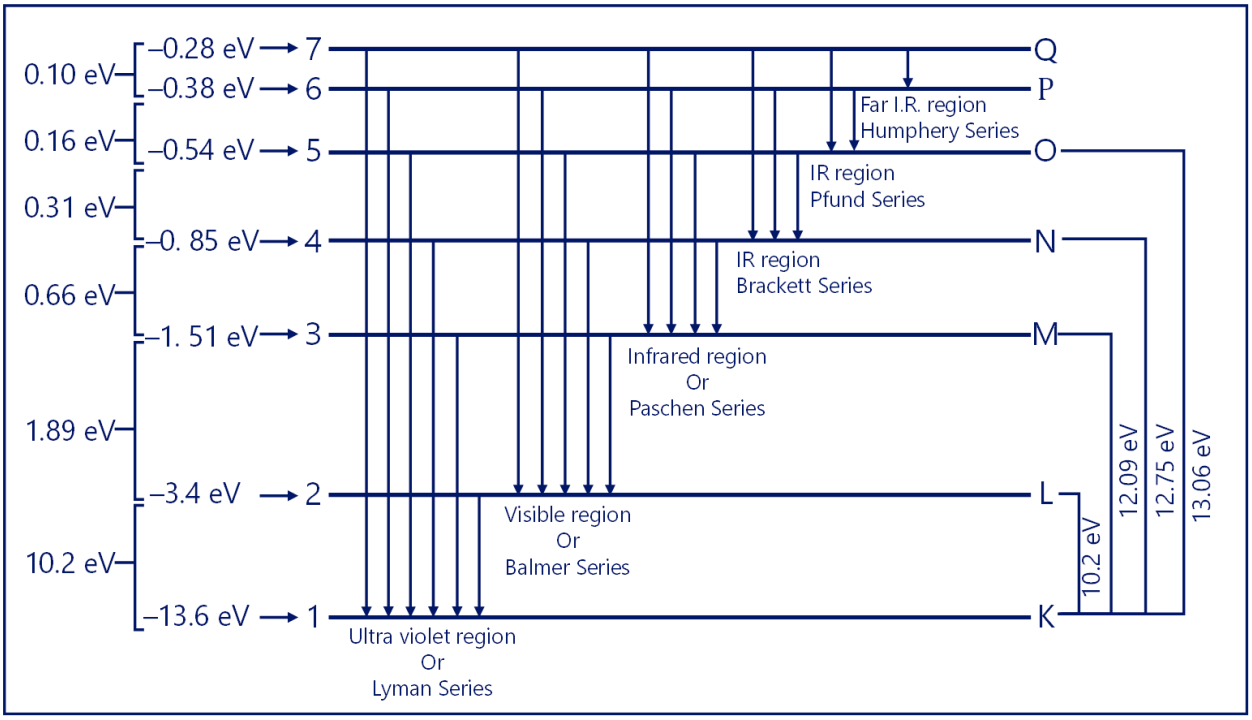


Hydrogen spectrum

When an electric excitation is applied on hydrogen atomic gas at low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a spectrum of several isolated sharp lines is obtained. The wavelength of various lines show that spectrum lines lie in Visible, Ultraviolet and Infra red region. These lines are grouped into different series.

TG: @Chalnaayaaar

Series	Discovered by	regions	$n_2 \rightarrow n_1$	No. of lines
Lyman	Lyman	U.V. region	$n_2 = 2,3,4 \ldots / n_1 = 1$	$n_2 - 1$
Balmer	Balmer	Visible region	$n_2 = 3,4,5 \ldots / n_1 = 2$	$n_2 - 2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4,5,6 \ldots / n_1 = 3$	$n_2 - 3$
Brackett	Brackett	I.R. region	$n_2 = 5,6,7 \ldots / n_1 = 4$	$n_2 - 4$
Pfund	Pfund	I.R. region	$n_2 = 6,7,8 \ldots / n_1 = 5$	$n_2 - 5$
Humphery	Humphery	Far I.R. region	$n_2 = 7,8,9 \ldots / n_1 = 6$	$n_2 - 6$



Similar words

- First line / Starting line / Initial line ($\lambda_{max.}$ and ν_{min})
- Last line / limiting line / marginal line ($\lambda_{min.}$ and ν_{max})
- First line of any series = α line
  Second line of any series = β line
  Third line of any series = γ line

Calculation of number of spectral lines

(a) Total number of spectral lines = $1 + 2 + \ldots (n_2 - n_1) = \dfrac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

Where: n_2 = higher energy level; n_1 = lower energy level

If $n_1 = 1$ (ground state)

Total number of spectral lines = $\dfrac{(n_2 - 1)n_2}{2} = \dfrac{n(n-1)}{2}$

(b) Number of spectral lines which falls in a particular series = $(n_2 - n_1)$

where n_2 = higher energy level, n_1 = Fixed lower energy level of each series.

TG: @Chalnaayaaar

Illustration 25:

In a hydrogen spectrum if electron moves from 7 to 1 orbit by transition in multi steps then find out the total number of lines in the spectrum.

Solution:

Lyman = $(n_2 - 1) = 7 - 1 = 6$

Balmer = $(n_2 - 2) = 7 - 2 = 5$

Paschen = $(n_2 - 3) = 7 - 3 = 4$

Brackett = $(n_2 - 4) = 7 - 4 = 3$

Pfund = $(n_2 - 5) = 7 - 5 = 2$

Humphrey = $(n_2 - 6) = 7 - 6 = 1$

Total = 21

Total number of lines can be calculated as follows:

$$\text{Total number of lines} = \frac{(n_2 - n_1)\left[(n_2 - n_1)+1\right]}{2} = \frac{(7-1)(6+1)}{2} = \frac{42}{2} = 21$$

Illustration 26:

In a hydrogen spectrum if electron moves from 6^{th} to 2^{nd} orbit by transition in multi steps then find out the number of lines in spectrum

Solution:

Total number of line = 4 + 3 + 2 + 1 = 10

or $$\text{Total number of lines} = \frac{(n_2 - n_1)\left[(n_2 - n_1)+1\right]}{2} = \frac{(6-2)(4+1)}{2} = \frac{4\times5}{2} = 10$$

Illustration 27:

In H atom if the electron moves from n^{th} orbit to 1^{st} orbit by transition in multi steps, then the total number of lines observed in the spectrum are 10, then find out the value of n.

Solution:

$$\text{Total number of lines} = \frac{(n_2 - n_1)\left[(n_2 - n_1)+1\right]}{2}$$

So, $$10 = \frac{(n-1)(n-1+1)}{2}$$

or $20 = (n - 1)(n)$

$n^2 - n - 20 = 0$

$n^2 - 5n + 4n - 20 = 0$

$n(n - 5) + 4(n - 5) = 0$

$(n + 4)(n - 5) = 0 \Rightarrow n = 5$

TG: @Chalnaayaaar

Rydberg Formula

In 1890, Rydberg gave a very simple theoretical equation for the calculation of the wavelength of various spectral of single electronic species.

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where R = Rydberg constant = 109678 cm^{-1} = 109700 cm^{-1} = 10970000 m^{-1} = 1.1 × 10^7 m^{-1}

$\frac{1}{R}$ = 9.12 × 10^{-6} cm = 912 Å

Derivation of Rydberg formula:

$\Delta E = E_{n_2} - E_{n_1}$

$$\Delta E = \frac{-2\pi^2 mK^2Z^2e^4}{n_2^2h^2} - \left[\frac{-2\pi^2 mK^2Z^2e^4}{n_1^2h^2}\right]$$

$$= \frac{2\pi^2 mK^2Z^2e^4}{n_1^2h^2} - \frac{2\pi^2 mK^2Z^2e^4}{n_2^2h^2} \qquad \left(\because \Delta E = h\nu = \frac{hc}{\lambda}\right)$$

$$\frac{hc}{\lambda} = \frac{2\pi^2 mK^2Z^2e^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{or} \quad \frac{1}{\lambda} = \frac{2\pi^2 mK^2e^4Z^2}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where $\frac{2\pi^2 mK^2e^4}{ch^3}$ is a constant which is equal to Rydberg is constant (R).

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Illustration 28:

Calculate the wavelength of 1st line of Balmer series in Hydrogen spectrum.

Solution:

For first line of Balmer series $n_1 = 2, n_2 = 3$

$$\frac{1}{\lambda} = R(1)^2\left[\frac{1}{4} - \frac{1}{9}\right] = R\left[\frac{9-4}{36}\right] = R\left[\frac{5}{36}\right]$$

$$\Rightarrow \lambda = \frac{36}{5R} = \frac{36}{5} \times \frac{1}{R} = \frac{36}{5} \times 9.12 \times 10^{-6} \text{ cm} = 65.66 \times 10^{-6} \text{ cm} = 6566 \text{ Å}$$

Illustration 29:

Calculate the frequency of the last line of the Lyman series in hydrogen spectrum.

Solution:

For last line of Lyman series $n_1 = 1, n_2 = \infty$

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{1} - 0\right) = R$$

$$\Rightarrow \upsilon = \frac{c}{\lambda} = c \times \frac{1}{\lambda} = c \times R = 3 \times 10^{10} \text{ cm s}^{-1} \times 109678 \text{ cm}^{-1} = 3.29 \times 10^{15} \text{ s}^{-1}$$

TG: @Chalnaayaaar

Illustration 30:

The wave number of 1st line of Balmer series of hydrogen spectrum is 15200 cm^{-1}. The wave number of 1st line of Balmer series of Li^{+2} spectrum will be?

Solution:

Wave number of Ist line of Balmer series of hydrogen spectrum. $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(for H, Z = 1) $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 15200\ cm^{-1}$

Wave number of Ist line of Balmer series of Li^{+2} ion is.

$\bar{\nu} = Z^2 \times R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ $\{\because Z = 3 \text{ for } Li^{+2}\}$

$\therefore\ \bar{\nu} = 3^2 \times 15200 = 9 \times 15200 = 136800\ cm^{-1}$

Illustration 31:

Calculate the ratio of maximum λ of Lyman & Balmer series?

Solution:

$E \propto \nu \propto \frac{1}{\lambda}$

$$\frac{\text{Maximum } \lambda \text{ of Lyman series}}{\text{Maximum } \lambda \text{ of Balmer series}} = \frac{1^{st} \text{ line of Lyman series}}{1^{st} \text{ line of Balmer series}}$$

$$\frac{\lambda_{Lyman}}{\lambda_{Balmer}} = \frac{\frac{1}{\lambda_B}}{\frac{1}{\lambda_L}} = \frac{R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]}{R\left[\frac{1}{1^2} - \frac{1}{2^2}\right]} = \frac{\frac{1}{4} - \frac{1}{9}}{\frac{1}{1} - \frac{1}{4}} = \frac{\frac{5}{36}}{\frac{3}{4}} = \frac{5}{36} \times \frac{4}{3} = \frac{5}{27}$$

Limitations of the Bohr's model:

(1) Bohr's theory does not explain the spectrum of multi electron atom/ion.

(2) Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.

(3) Bohr inter related quantum theory of radiation and classical laws of physics without any theoretical explanation.

(4) Bohr's theory does not explain the fine structure of the spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by spectroscope of more resolution power.

(5) Bohr's theory does not explain the splitting of spectral lines in the presence of magnetic field (Zeeman's effect) or electric field (Stark effect)

TG: @Chalnaayaaar

BEGINNER'S BOX-4

1. The line spectra of two elements are not identical because
(1) The elements don't have the same number of neutrons.
(2) They have different mass numbers
(3) Their outermost electrons are at different energy levels.
(4) They have different valences.

2. In which of the following transition will the wavelength be minimum.
(1) n = 6 to n = 4 (2) n = 4 to n = 2 (3) n = 3 to n = 1 (4) n = 2 to n =1

3. The wavelength of third line of the Balmer series for a H atom is
(1) $\frac{21}{100R}$ (2) $\frac{100}{21R}$ (3) $\frac{21R}{100}$ (4) $\frac{100R}{21}$

4. When the electron of a hydrogen atom jumps from n = 4 to n = 1 state, the number of spectral lines emitted is
(1) 15 (2) 6 (3) 3 (4) 4

Wave Mechanical Model of an Atom

This model consists of following
(A) de-Broglie concept (Dual nature of Matter)
(B) Heisenberg's Uncertainty principle.

The Dual Nature of Matter (The Wave Nature of Electron)

In 1924, a French physicist, Louis de-Broglie suggested that if the nature of light is both that of a particle and of a wave, then this dual behaviour should be true also for the matter.

(1) The wave nature of light rays and X-rays is proved on the basis of their interference and diffraction and many facts related to radiations can only be explained when the beam of light rays is regarded as composed of energy particles or photons whose velocity is 3×10^{10} cm/s.

(2) According to de-Broglie, the wavelength λ of an electron is inversely proportional to its momentum p.

$\lambda \propto \frac{1}{p}$ or $\lambda = \frac{h}{p}$ (Here h = Planck's constant, p = momentum of electron)

$\because$ Momentum (p) = Mass (m) × Velocity (v) $\therefore$ $\lambda = \frac{h}{mv}$

(3) The above relation can be proved as follows by using Einstein's equation, Planck's quantum theory and wave theory of light.
Einstein's equation, $E = mc^2$ where E is energy, m is mass of a body and c is its velocity.

$\because E = h\nu = h \times \frac{c}{\lambda}$ (According to Planck's quantum theory) ...(i)

and $c = \nu\lambda$ (According to wave theory of light) $\therefore \nu = \frac{c}{\lambda}$

But according to Einstein's equation, $E = mc^2$ ...(ii)

From equation (i) & (ii): $mc^2 = h \times \frac{c}{\lambda}$ or $mc = \frac{h}{\lambda}$ or $p = \frac{h}{\lambda}$ or $\lambda = \frac{h}{p}$

TG: @Chalnaayaaar

(4) It is clear from the above equation that the value of λ decreases on increasing either m or v or both. The wavelength of many fast-moving objects like an aeroplane or a cricket ball, is very low because of their high mass.

Bohr's theory and de-broglie concept:

(1) According to de-Broglie, the nature of an electron moving around the nucleus is like a wave that flows in circular orbits around the nucleus.

(2) If an electron is regarded as a wave, the quantum condition as given by Bohr in his theory is readily fulfilled.

(3) If the radius of a circular orbit is r, then its circumference will be $2\pi r$.

(4) We know that according to Bohr theory, $mvr = \frac{nh}{2\pi}$

or $2\pi r = \frac{nh}{mv}$ ($\because$ mv = p momentum)

or $2\pi r = \frac{nh}{p}$ $\left(\because \frac{h}{p} = \lambda \text{ de-Broglie equation}\right)$

$\therefore$ $2\pi r = n\lambda$ (where n = total number of waves 1, 2, 3, 4, 5, ...∞ and λ = Wavelength

(5) $\because 2\pi r = \frac{nh}{mv}$ or $mvr = \frac{nh}{2\pi}$ $\because$ mvr = Angular momentum

Thus mvr = Angular momentum, which is a integral multiple of $\frac{h}{2\pi}$.

(6) It is clear from the above description that according to de-Broglie there is similarity between wave theory and Bohr theory.

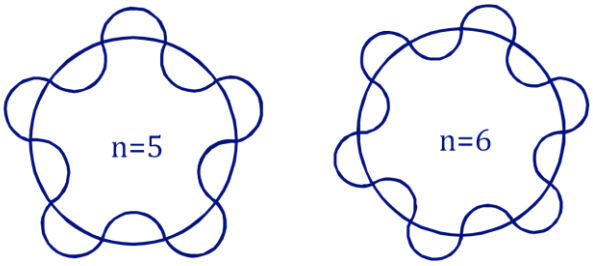


Figure : Similarity between de-Broglie waves and Bohr's orbit

★ Golden Key Points ★

de-Broglie wavelength in terms of kinetic energy.

Kinetic Energy (K.E.) = $\frac{1}{2}mv^2$ or $m \times K.E. = \frac{1}{2}m^2v^2$ or $m^2v^2 = 2m\ K.E.$ or $mv = \sqrt{2m\ K.E.}$

But = $\lambda = \frac{h}{mv}$ $\therefore \lambda = \frac{h}{\sqrt{2m\,K.E.}}$ $\left(\because mv = \sqrt{2m\ K.E.}\right)$

When a charged particle carrying Q coulomb charge is accelerated by applying potential difference of V volts, then:

K.E. = Q × V Joule

TG: @Chalnaayaaar

But $\lambda = \frac{h}{\sqrt{2m\,K.E.}}$ $\therefore \lambda = \frac{h}{\sqrt{2m\,QV}}$

For electron $\left(\lambda = \sqrt{\frac{150}{V}}\ \text{Å}\right) = \frac{12.25}{\sqrt{V}}\text{Å}$

The wave nature of electron was verified experimentally by Davisson and Germer.

de-Broglie hypothesis is applicable to macroscopic as well as microscopic objects but it has no physical significance for macroscopic objects.

Illustration 32:

The mass of a particle is 1 mg and its velocity is 4.5×10^5 cm per second. What should be the wavelength of this particle if h = 6.625×10^{-27} erg second.

(1) 1.4722×10^{-24} cm (2) 1.4722×10^{-29} cm

(3) 1.4722×10^{-32} cm (4) 1.4722×10^{-34} cm

Solution:

Given that m = 1 mg = 1×10^{-3} g, v = 4.5×10^5 cm s^{-1}, h = 6.625×10^{-27} erg s.

$\therefore \lambda = \frac{h}{mv} = \frac{6.625\times10^{-27}\,\text{ergs}}{1\times10^{-3}\,\text{g}\times4.5\times10^{5}\,\text{cms}^{-1}} = 1.4722 \times 10^{-29}$ cm

Illustration 33:

Which of the following should be the wavelength of an electron if its mass is 9.1×10^{-31} kg and its velocity is 1/10th of that of light and the value of his 6.6252×10^{-34} joule second?

(1) 2.446×10^{-7} metre (2) 2.246×10^{-9} metre

(3) 2.246×10^{-11} metre (4) 2.246×10^{-13} metre

Solution:

Given that m = 9.1×10^{-31} kg, v = $\frac{1}{10}$ of velocity of light

or $v = \frac{1}{10} \times 3 \times 10^8$ metre $second^{-1}$ i.e. 3×10^7 metre $second^{-1}$

h = 6.6252×10^{-34} joule second

$\lambda = \frac{h}{mv} = \frac{6.6252\times10^{-34}\,\text{J.s}}{9.1\times10^{-31}\,\text{kg}\times3\times10^{7}\,\text{ms}^{-1}} = \frac{6.6252\times10^{-34}}{27.3\times10^{-24}}$

$= 0.2426 \times 10^{-10}$ metre $= 2.426 \times 10^{-11}$ metre

Illustration 34:

A ball weighing 25 g moves with a velocity of 6.6×10^4 cm s^{-1} then find out the de-Broglie wavelength associated with it.

Solution:

$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}\times10^{7}\,\text{ergs}}{25\times6.6\times10^{4}\,\text{cms}^{-1}} = 0.04 \times 10^{-31}$ cm $= 4 \times 10^{-33}$ cm

Heisenberg's uncertainty principle

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not

TG: @Chalnaayaaar

possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave extends throughout a region of space.

In 1927, Werner Heisenberg presented a principle known as Heisenberg's uncertainty principle which states that: "It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."

The uncertainty in measurement of position, (Δx), and the uncertainty in momentum (Δp) are related by Heisenberg's relationship as

$$\Delta x.\Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x.\, m\Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x.\Delta v \geq \frac{h}{4\pi m} \quad \text{or} \quad \Delta t \times \Delta x \times \frac{\Delta p}{\Delta t} \geq \frac{h}{4\pi}$$

$$F \times \Delta t \times \Delta x \geq \text{ or } \Delta E \times \Delta t \geq \frac{h}{4\pi}$$

where h is Planck's constant.

(i) When $\Delta x = 0$, $\Delta v = \infty$

(ii) When $\Delta v = 0$, $\Delta x = \infty$ So, if the position is known quite accurately, i.e., Δx is very small, Δv becomes large and vice-versa.

Illustration 35:

If the uncertainty in position of a moving particle is 0 then find out Δp –

Solution:

$$\Delta x\, \Delta p = \frac{h}{4\pi} \quad \text{or} \quad \Delta p = \frac{h}{4\pi\Delta x} \quad \text{or} \quad \Delta p = \frac{h}{4\pi\times 0} \quad \text{or} \quad \Delta p = \infty$$

Illustration 36:

Calculate the uncertainty in the position of a particle when the uncertainty in momentum is

(a) 1×10^{-3} g cm s^{-1} (b) zero.

Solution:

(a) Given $\Delta p = 1 \times 10^{-3}$ g cm s^{-1}, $h = 6.62 \times 10^{-27}$ erg s, $\pi = 3.142$

According to Heisenberg's uncertainty principle

$$\Delta x.\Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \geq \frac{h}{4\pi}.\frac{1}{\Delta p} \geq \frac{6.62\times 10^{-27}}{4\times 3.142} \times \frac{1}{10^{-3}} \geq 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of Δx will be infinity.

Illustration 37:

The uncertainty in position and velocity of a particle are 10^{-10} m and 5.27×10^{-24} ms^{-1} respectively. Calculate the mass of the particle ($h = 6.625 \times 10^{-34}$ joule second)

Solution:

According to Heisenberg's uncertainty principle,

$$\Delta x.m\,\Delta v = \frac{h}{4\pi} \quad \text{or} \quad m = \frac{h}{4\pi\Delta x.\Delta v} = \frac{6.625\times 10^{-34}}{4\times 3.143\times 10^{-10}\times 5.27\times 10^{-24}} = 0.099 \text{ kg}$$

Illustration 38:

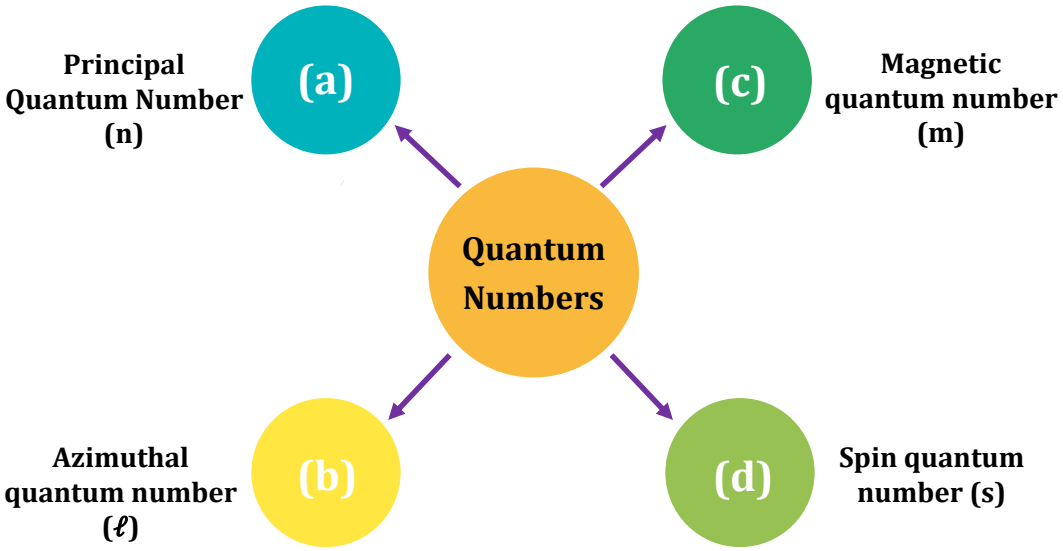
Calculate the uncertainty in velocity of a cricket ball of mass 150 g if the uncertainty in its position is of the order of 1Å ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}).

Solution:

$$\Delta x.\, m\, \Delta v = \frac{h}{4\pi} \quad \text{or} \quad \Delta v = \frac{h}{4\pi \Delta x.m} = \frac{6.6\times10^{-34}}{4\times3.143\times10^{-10}\times0.150} = 3.499 \times 10^{-24}\ ms^{-1}$$

Quantum Numbers

To obtain complete information about an electron in an atom 4 identification numbers are required and these identification numbers are called as quantum numbers.



(a) Principal Quantum Number (n)

Given By → Bohr

- It represents the name and energy of the shell to which electron belongs and size of orbit.
- The value of n lies between 1 to ∞

  i.e n = 1,2,3,4– – – – – ∞ corresponding name of shells are K, L, M, N, O, – – – – –
- Greater the value of n, greater is the distance from the nucleus.

  $r = 0.529 \times \frac{n^2}{Z}$ Å

  $r_1 < r_2 < r_3 < r_4 < r_5$ – – – – – – – – –
- Greater the value of n, greater is the energy of shell

  $E = -13.6 \times \frac{Z^2}{n^2}$ eV/atom

  $E_1 < E_2 < E_3 < E_4$ – – – – – – – – –
- Velocity of electron $v = 2.18 \times 10^6 \frac{Z}{n}$ m/s

  $v_1 > v_2 > v_3$ .....
- The angular momentum of a revolving electron is $mvr = \frac{nh}{2\pi}$

  Where n = Principal quantum number.
- The number of electrons in a particular shell is equal to $2n^2$

(b) Azimuthal quantum number/Angular quantum number/Secondary quantum number /Subsidiary quantum number (ℓ)

Given by – Sommerfeld

- It represents the name of the subshell, shape of orbital and orbital angular momentum
- Possible values of 'ℓ' are :-

i.e. $\ell = 0, 1, 2$ ---------- (n–1)

$\ell = 0 \rightarrow$ s Subshell
$\ell = 1 \rightarrow$ p Subshell
$\ell = 2 \rightarrow$ d Subshell
$\ell = 3 \rightarrow$ f Subshell

- Value of ℓ lies between 0 to (n – 1) in a particular n^{th} shell :-

Ex. If n = 1 then $\ell = 0 \Rightarrow$ 1s i.e. in n =1 shell, only one subshell 's' is present.

If n = 2 then $\ell = 0,1 \Rightarrow$ 2s, 2p i.e. in n =2 shell, two subshells 's' & 'p' are present.

If n = 3 then $\ell = 0, 1, 2 \Rightarrow$ 3s, 3p, 3d i.e. in n =3 shell, three subshells 's', 'p' & 'd' are present.

If n = 4 then $\ell = 0,1, 2, 3 \Rightarrow$ 4s, 4p, 4d, 4f i.e. in n = 4 shell, four subshells 's', 'p' , 'd' & 'f' are present.

- If the value of n is same then the order of energy of the various subshells will be
s < p < d < f [valid only for multi-electron species]
Ex. 4s < 4p < 4d < 4 f, 3s < 3p < 3d, 2s < 2p
- If Value of ℓ is same but value of n is different then the order of energy will be.

Ex. 1s < 2s < 3s < 4s < 5s < 6s
3d < 4d < 5d < 6d
4p < 5p < 6p

- The orbital angular momentum = $\sqrt{\ell(\ell+1)}\,\frac{h}{2\pi}$ or $\sqrt{\ell(\ell+1)}\,\hbar$ $\left\{\because \hbar = \frac{h}{2\pi}\right\}$ {$\hbar$ is called as 'hash' }

Orbital angular momentum: For s subshell = 0

For p subshell = $\sqrt{2}\,\frac{h}{2\pi}$ or $\sqrt{2}\,\hbar$

- The number of electrons in a particular subshell is equal to $2(2\ell+1)$

for s subshell number of electrons = 2 e^-
for p subshell number of electrons = 6 e^-
for d subshell number of electrons = 10 e^-
for f subshell number of electrons = 14 e^-

- Shape of the orbital:

s $\rightarrow$ Spherical shape
p $\rightarrow$ Dumb Bell shape
d $\rightarrow$ Double Dumb Bell shape
f $\rightarrow$ Complex shape

TG: @Chalnaayaaar

BEGINNER'S BOX-5

1. de-Broglie wavelength for electron is related to applied voltage as :-

(1) $\lambda = \frac{12.3}{\sqrt{h}}$ Å (2) $\lambda = \frac{12.3}{\sqrt{V}}$ Å (3) $\lambda = \frac{12.3}{\sqrt{r}}$ Å (4) $\lambda = \frac{12.3}{\sqrt{m}}$ Å

2. Select the incorrect relation among the following.

(1) $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ (2) $\Delta x \cdot \Delta p \geq \frac{h}{4\pi m}$ (3) $\Delta x \cdot \Delta V \geq \frac{h}{4\pi m}$ (4) $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

3. If the kinetic energy of an electron is increased 4 times, the wavelength of the de-Broglie wave associated with it would become :-

(1) four times (2) two times (3) half times (4) one fourth times

4. Velocity of de-Broglie wave is given by :-

(1) $\frac{c^2}{\nu}$ (2) $\frac{h\nu}{mc}$ (3) $\frac{mc^2}{h}$ (4) $\frac{\nu}{\lambda}$

5. The representation of an orbital with n = 4 and ℓ =1 :-

(1) 4d (2) 4s (3) 4f (4) 4p

6. Maximum number of electrons present in M shell is :-

(1) 8 (2) 18 (3) 32 (4) 10

(c) Magnetic Quantum Number /Orientation Quantum Number (m):

Given by **Linde**

- It represents the orientation of electron cloud (orbital)
- Under the influence of magnetic field each subshell is further subdivided into orbitals (The electron cloud is known as orbital)

  Magnetic quantum number describe these different distributions of electron cloud.
- Value of m = all integral value from $-\ell$ to $+\ell$ including zero.

  i.e. Value of m = $-\ell$ to $+\ell$

(d) Spin Quantum number (s):

Given by **Goudsmit** and **Uhlenbeck**

- It represents the direction of electron spin around its own axis
- For clockwise spin/spin up ($\uparrow$) electron $\rightarrow \pm 1/2$
- For anti-clockwise spin/spin down ($\downarrow$) electron $\rightarrow \mp 1/2$

  Spin angular momentum of an electron = $\sqrt{s(s+1)}.\frac{h}{2\pi}$ or $\sqrt{s(s+1)}\hbar$
- Each orbital can accomodate 2 electrons with opposite spin or spin paired.

  Correct $\boxed{\uparrow\downarrow}$ Spin paired e^-

  Wrong $\boxed{\uparrow\uparrow}$ Spin parallel e^-

TG: @Chalnaayaaar

Orbital: 3D space around the nucleus where the probability of finding electrons is maximum is called an orbital. An orbital can be represented by 3 set of quantum numbers

$= \Psi_{n, \ell, m}$

Ex. 1 : $2p_x$; n = 2, ℓ = 1, m = –1 or m = +1

Ex. 2 : $3d_{z^2}$; n = 3, ℓ = 2, m = 0

Ex. 3 : $\Psi_{(3,2,0)}$; n = 3, ℓ = 2, m = 0; $3d_{z^2}$

Illustration 39:

Calculate the value of n, ℓ and m for 3s orbital ?

Solution:

n = 3, ℓ = 0, m = 0

Illustration 40:

Which of the following set of quantum numbers is not possible ?

(a) n = 2, ℓ = 0, m – 1, $s = -\frac{1}{2}$ (b) n = 3, ℓ = 2, m = 0, $s = \pm\frac{1}{2}$ (c) n = 2, ℓ = 3, m = – 2, $s = \pm\frac{1}{2}$

Solution:

(a) not possible (b) possible (c) not possible

Node: It is point /line / plane / surface in which probability of finding electron is zero.

Total node = n – 1

They are of 2 types.

(i) Number of Radial nodes / Spherical nodes / Nodal surface in an orbital = n – ℓ – 1

(ii) Number of Angular nodes / Nodal planes in an orbital = ℓ

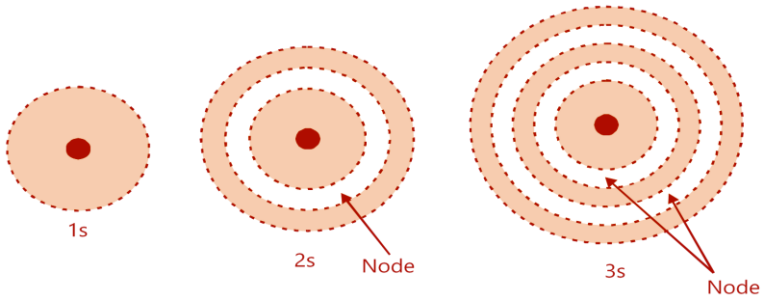
* Nucleus and ∞ (infinite) are not considered as node.

Types of orbitals:

Case-I: If ℓ = 0 then m = 0, it implies that s subshell has only one orbital called as s orbital.

Shape of s-orbitals:

The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding electron is same in all directions from the nucleus. The size of the orbital depends on the value of principal quantum number. The 1s orbital is smaller than 2s-orbital and 2s-orbital is smaller than 3s-orbital, but all are spherical in shape as shown in figure.

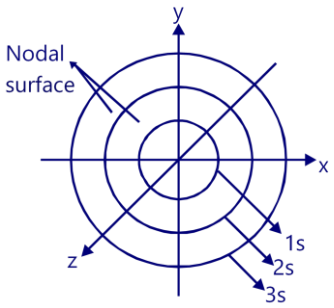


Although the s-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below:

TG: @Chalnaayaaar

(i) The probability of finding 1s electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2s electrons, the probability is again maximum near the nucleus and then decreases to zero as the distance from the nucleus increases. The intermediate region (a spherical shell) where the probability is zero is called a nodal surface or simply node. Thus, 2s-orbital differs from 1s-orbital in having one node within it. Similarly, 3s has two nodes. In general, any ns orbital has (n -1) nodes.

(ii) The size and energy of the s-orbital increases as the principal quantum number increases, i.e., the size and energy of s-orbital increases in the order 1s < 2s < 3s ....



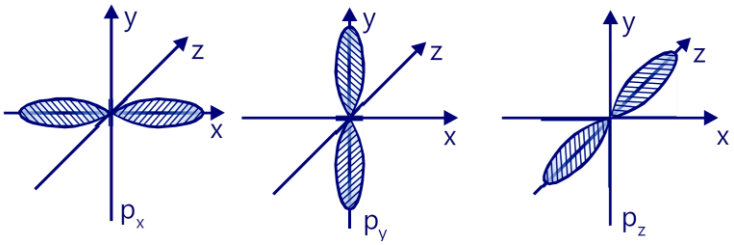
The s orbital of higher energy levels are also spherically symmetrical and can be represented as above

Case-II If $\ell = 1$ (p – subshell) then $m = \begin{array}{|c|c|c|}\hline -1 & 0 & +1 \\ \hline p_x & p_z & p_y \\ \hline \end{array}$

It implies that, p subshell have three orbitals called as p_x, p_y and p_z.

Shape of p-orbitals:

There are three p-orbitals, commonly referred to as p_x, p_y and p_z. These three p-orbitals, possess equivalent energy and therefore, have same relation with the nucleus. They, however, differ in their direction & distribution of the charge.



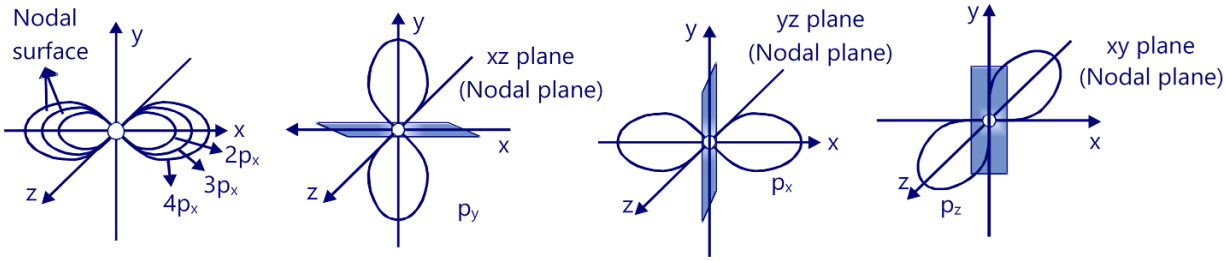
(figure)

These three p-orbitals are situated at right angle to one another and are directed along x, y and z axis

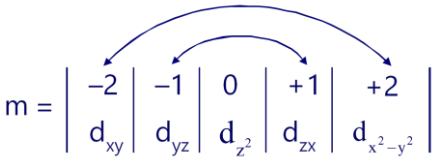
- Each p orbital has dumb bell shape (2 lobes which are separated from each other by nucleus).
- The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.
- Each p orbital of higher energy level are also dumb bell shape but they have nodal surface.

Nodal surface:		**Nodal Plane:**	
Orbital	Nodal surface	Orbital	Nodal plane
3 p_x	1	p_x	yz plane
4 p_x	2	p_y	xz plane
np_x	(n – 2)	p_z	xy plane

TG: @Chalnaayaaar

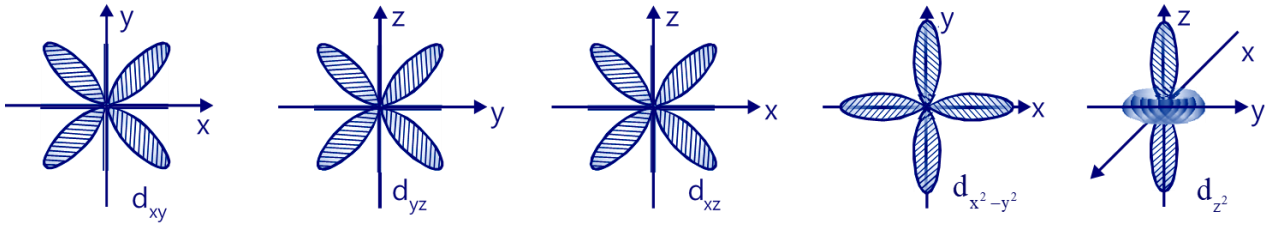


Case III When l = 2, 'm' has five values – 2, –1, 0, +1, +2. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals d_{xy}, d_{yz}, d_{xz}, contain four lobes while fifth orbital consists of only two lobes. The lobes of d_{xy} orbital lie between x and y axes. Similar is the case for d_{yz} and d_{xz}. Four lobes of orbital are lying along x and y axes while the two lobes of orbital are lying along z axis and contain a ring of negative charge surrounding the nucleus in xy plane. Geometry of d orbital is double dumbbell



Shape of d–orbitals:

It implies that d subshell has 5 orbitals i.e. five electron cloud and can be represented as follows



Each d-orbital of higher energy level also have double dumbbell shape but they also have nodal surface.

In d-orbitals:

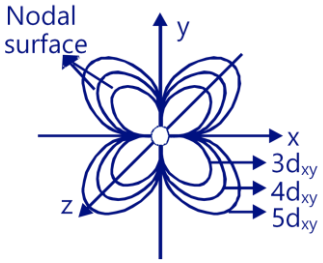
(i) Nodal Surface → $3\ d_{xy}$ → 0 Nodal surface

$4\ d_{xy}$ → 1 Nodal surface

$5\ d_{xy}$ → 2 Nodal surface

$n\ d_{xy}$ → (n – 3)

Number of nodal surface = $n - \ell - 1$



(ii) Nodal plane : d_{xy} → xz & yz nodal plane

d_{xz} → xy & zy nodal plane

d_{zy} → zx & yx nodal plane

$d_{x^2-y^2}$ → 2 nodal planes

d_{z^2} → 0 nodal plane

Note: Orbitals of d subshell are equivalent in energy.

Illustration 41:

Calculate the value of n, ℓ and m for $3p_z$ orbital?

Solution:

n = 3, ℓ= 1, m = 0

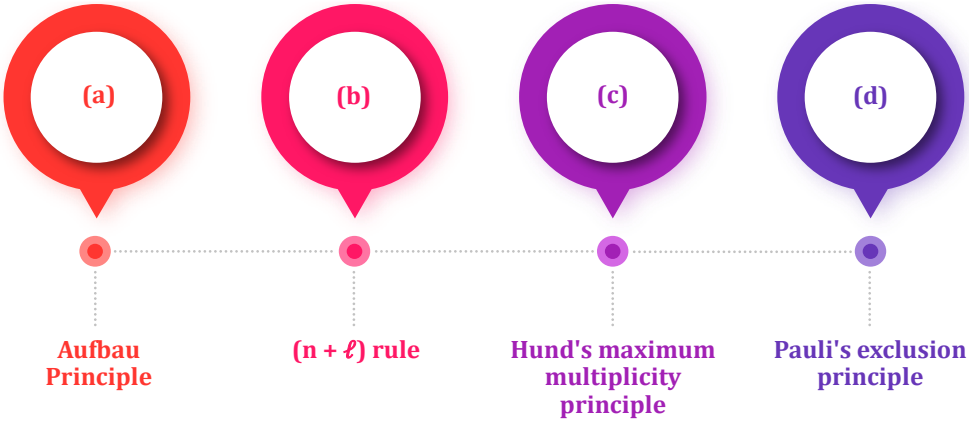
Illustration 42:

Calculate the value of n, ℓ, m for 3s orbital?

Solution:

n = 3, ℓ= 0, m = 0

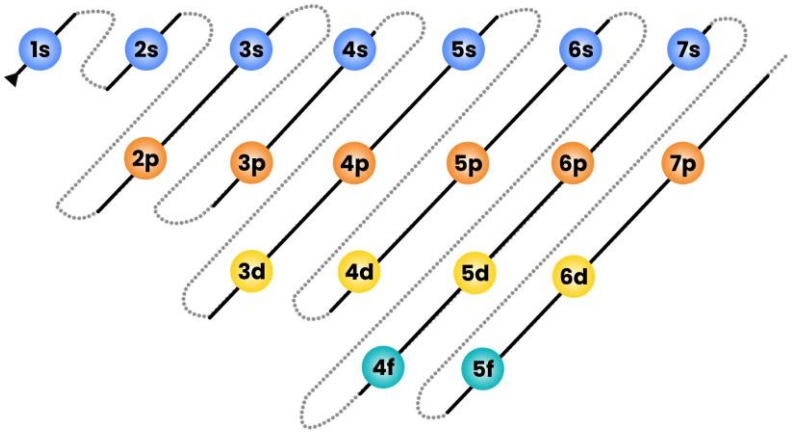
Rules for Filling of Electrons



(a) Aufbau Principle

Aufbau is a German word and its meaning is 'Building up'

- Aufbau principle gives a sequence in which various subshell are filled up depending on the relative order of the energies of various subshell.
- **Principle:** The subshell with minimum energy is filled up first when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.
- The sequence in which various subshell are filled are as follows.



$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, ...$

For Example

$_1H \rightarrow 1s^1$

$_2He \rightarrow 1s^2$

$_3Li \rightarrow 1s^2, 2s^1$

$_4Be \rightarrow 1s^2, 2s^2$

$_5B \rightarrow 1s^2, 2s^2, 2p^1$

$_6C \rightarrow 1s^2, 2s^2, 2p^2$

$_7N \rightarrow 1s^2, 2s^2, 2p^3$

$_8O \rightarrow 1s^2, 2s^2, 2p^4$

$_9F \rightarrow 1s^2, 2s^2, 2p^5$

$_{10}Ne \rightarrow 1s^2, 2s^2, 2p^6$

$_{11}Na \rightarrow 1s^2, 2s^2, 2p^6, 3s^1$

$_{12}Mg \rightarrow 1s^2, 2s^2, 2p^6, 3s^2$

$_{13}Al \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

$_{14}Si \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^2$

$_{15}P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

$_{16}S \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

$_{17}Cl \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

$_{18}Ar \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

$_{19}K \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

$_{20}Ca \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$

$_{21}Sc \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$

$_{22}Ti \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$

$_{23}V \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$

$_{24}Cr \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$ [Exception]

$_{25}Mn \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$

$_{26}Fe \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

$_{27}Co \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$

$_{28}Ni \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

$_{29}Cu \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$ [Exception]

$_{30}Zn \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

Electronic configuration can be written by following different methods:

$_{26}Fe \rightarrow$ (1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

(2) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

(3) $1s^2, 2s^2p^6, 3s^2p^6d^6, 4s^2$

2 8 14 2

(4) [Ar] $4s^2$ $3d^6$

$_{26}Fe \rightarrow 1s^2$ $\underbrace{2s^2\ 2p^6}_{(n-2)}\ \underbrace{3s^2\ 3p^6\ 3d^6}_{(n-1)}\ \underbrace{4s^2}_{n}$

n → Outer most Shell or Ultimate Shell or Valence Shell

In this Shell electrons are called as Valence electrons or this is called core charge

(n–1) → Penultimate Shell or core or pre valence Shell

(n–2) → Pre Penultimate Shell

If we remove the last 'n' Shell (ultimate Shell) then the remaining shells are collectively called as kernel.

Ex. $_{26}Fe \rightarrow \underbrace{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6}\ 4s^2$

(b) (n + ℓ) Rule (For multi electron species)

According to it the sequence in which various subshell are filled up can also be determined with the help of (n + ℓ) value for a given subshell.

Principle of (n+ℓ) rule:

The subshell with lowest (n + ℓ) value is filled up first. When two or more subshell have same (n+ℓ) value then the subshell with lowest value of n is filled up first.

In case of H-atom:

Energy only depends on principal quantum number

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < .....

Sub Shell	n	ℓ	n + ℓ	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	(1)
3s	3	0	3	(2)
3p	3	1	4	(1)
4s	4	0	4	(2)
3d	3	2	5	(1)
4p	4	1	5	(2)
5s	5	0	5	(3)
4d	4	2	6	(1)
5p	5	1	6	(2)
6s	6	0	6	(3)

Order: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}$, ...

(c) Hund's Maximum Multiplicity Rule (Multiplicity: Many of the same kind)

- This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals).
- It states : pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.
- Since there are three p, five d and seven *f* orbitals, therefore, the pairing of electrons will start in the p, d and *f* orbitals with the entry of 4th, 6th and 8th electron, respectively.

Ex. $_5B \rightarrow 1s^2\ 2s^2\ 2p^1$ ↑↓ ↑↓ ↑ | |

$_6C \rightarrow 1s^2\ 2s^2\ 2p^2$ ↑↓ ↑↓ ↑ ↑ |

$_7N \rightarrow 1s^2\ 2s^2\ 2p^3$ ↑↓ ↑↓ ↑ ↑ ↑

$_8O \rightarrow 1s^2\ 2s^2\ 2p^4$ ↑↓ ↑↓ ↑↓ ↑ ↑

$_9F \rightarrow 1s^2\ 2s^2\ 2p^5$ ↑↓ ↑↓ ↑↓ ↑↓ ↑

$_{10}Ne \rightarrow 1s^2\ 2s^2\ 2p^6$ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

(d) Pauli's Exclusion Principle

In 1925, Pauli stated that no two electrons in an atom can have same values of all four quantum numbers

i.e., an orbital can accommodate maximum 2 electrons with opposite spin.

Ex.1. $^{12}_{6}C \rightarrow$ $1s^2$ ↑↓ | $2s^2$ ↑↓ | $2p^2$ ↑ ↑ |

n	=	1	2	2
ℓ	=	0	0	1
m	=	0	0	+ 1, 0, –1
s	=	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},+\frac{1}{2}$

Ex.2 $_{17}Cl \rightarrow$ $1s^2$ ↑↓ | $2s^2$ ↑↓ | $2p^6$ ↑↓ ↑↓ ↑↓ | $3s^2$ ↑↓ | $3p^5$ ↑↓ ↑↓ ↑

n	=	1	2	2	3	3
ℓ	=	0	0	1	0	1
m	=	0	0	+1,–1, 0	0	+1, –1, 0
s	=	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}+\frac{1}{2},-\frac{1}{2}+\frac{1}{2},-\frac{1}{2}$		$+\frac{1}{2},-\frac{1}{2}+\frac{1}{2},-\frac{1}{2}+\frac{1}{2}$

Exception of Aufbau principle:

In some cases it is seen that the electronic configuration is slightly different from the arrangement given by Aufbau principle. A simple reason behind this is that half filled & full filled subshell have got extra stability.

Ex.1 $_{24}Cr \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$ (wrong configuration)

↑↓ | ↑ ↑ ↑ ↑ |

$_{24}Cr \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$ (correct configuration)

↑ | ↑ ↑ ↑ ↑ ↑

Ex.2 $_{29}Cu \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$ (wrong configuration)

↑↓ | ↑↓ ↑↓ ↑↓ ↑↓ ↑

$_{29}Cu \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$ (correct configuration)

↑ | ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

Illustration 43:

Calculate the number of unpaired electrons in Cr

Solution:

$_{24}Cr \rightarrow$ $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$ $3d^5$

In $_{24}Cr$, 6 electrons are unpaired.

Illustration 44:

Calculate the number of unpaired electrons in Cr^{+3}

Solution:

$Cr^{+3} \rightarrow$ $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^0$ $3d^3$

in Cr^{+3}, 3 electrons are unpaired.

Some Special Point:

1. Total spin = $\pm\left(\frac{1}{2}\right)\times$ no. of unpaired e^-
2. Magnetic moment (μ) = $\sqrt{n(n+2)}$ B.M.

   Where 'n' is no. of unpaired electron
3. Paramagnetic: Those species which contain one or more than one unpaired electron.
4. Diamagnetic: Those species which do not contain any unpaired electron.

Configuration of Ion:

(a) First we have to write the configuration of atom in its ground state.

(b) Now, based upon the charge present on the atom we have to remove or add electron in its valence shell.

Na^+: (a) Na $\rightarrow$ $1s^2, 2s^22p^6, 3s^1$

(b) Na^+ $\rightarrow$ $1s^2, 2s^22p^6$

Cr^+: (a) Cr $\rightarrow$ $1s^2, 2s^22p^6, 3s^23p^6, 4s^1, 3d^5$

(b) Cr^+ $\rightarrow$ $1s^2, 2s^22p^6, 3s^23p^6\ 3d^5$

Cr^{+2} $\rightarrow$ $1s^2, 2s^22p^6, 3s^23p^6\ 3d^4$

Cr^{+3} $\rightarrow$ $1s^2, 2s^22p^6, 3s^23p^6\ 3d^3$

Fe^{+2}: Fe $\rightarrow$ $1s^2, 2s^22p^6, 3s^23p^64s^23d^6$

Fe^{+2} $\rightarrow$ $1s^2, 2s^22p^6, 3s^23p^64s^03d^6$

Illustration 45:

Calculate the number of unpaired electrons in 3d subshell of Cr^{+3}

Solution:

3

Illustration 46:

Calculate the number of unpaired electrons in Fe^{+2} & Fe^{+3}

Solution:

$Fe^{+2} \rightarrow$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^6$ = 4 unpaired electrons

$Fe^{+3} \rightarrow$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$ = 5 unpaired electrons

BEGINNER'S BOX-6

1. A neutral atom of an element has 2K, 8L, 11 M and 2N electrons. The number of p-electrons in the atom are :-
(1) 2 (2) 12 (3) 10 (4) 6

2. An atom has 2 electrons in K–shell, 8 electrons in L–shell & 8 electrons in M–shell. The number of p–electrons presents in the element is :–
(1) 10 (2) 7 (3) 12 (4) 4

3. The maximum number of such electrons in an atom with quantum number n = 3, ℓ = 2 is :-
(1) 2 (2) 6 (3) 10 (4) 14

4. The number of orbitals in n=3 are :-
(1) 1 (2) 4 (3) 9 (4) 16

5. In potassium the probable order of energy level for 19^{th} electron is :-
(1) 3s > 3d (2) 4s < 3d (3) 4s > 4p (4) 4s = 3d

BEGINNER'S BOX ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7
	Ans.	**3**	**3**	**2**	**4**	**4**	**4**	**2**

BEGINNER'S BOX-2	Que.	1	2	3
	Ans.	**3**	**1**	**2**

BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7
	Ans.	**3**	**4**	**3**	**2**	**2**	**3**	**1**

BEGINNER'S BOX-4	Que.	1	2	3	4
	Ans.	**3**	**3**	**2**	**2**

BEGINNER'S BOX-5	Que.	1	2	3	4	5	6
	Ans.	**2**	**2**	**3**	**2**	**4**	**2**

BEGINNER'S BOX-6	Que.	1	2	3	4	5
	Ans.	**2**	**3**	**3**	**3**	**2**